

## Chapter 4 Viscoelasticity

### 4.1 Introduction

- ▶ Glassy state of polymer = elastic (more likely)  
*Instantaneous deformation + perfect recovery upon removal of stress at small strain*
- ▶ Melt state of polymer = viscous (more likely)  
*Needs time for deformation and no recovery*
- ▶ Rubbery state of polymer (not crosslinked ones) = viscoelastic  
*Partially flow, partially recovered, more importantly time dependent*

See Figure 4.21 for  $G$  vs  $T$  relationships for three representative engineering polymers.

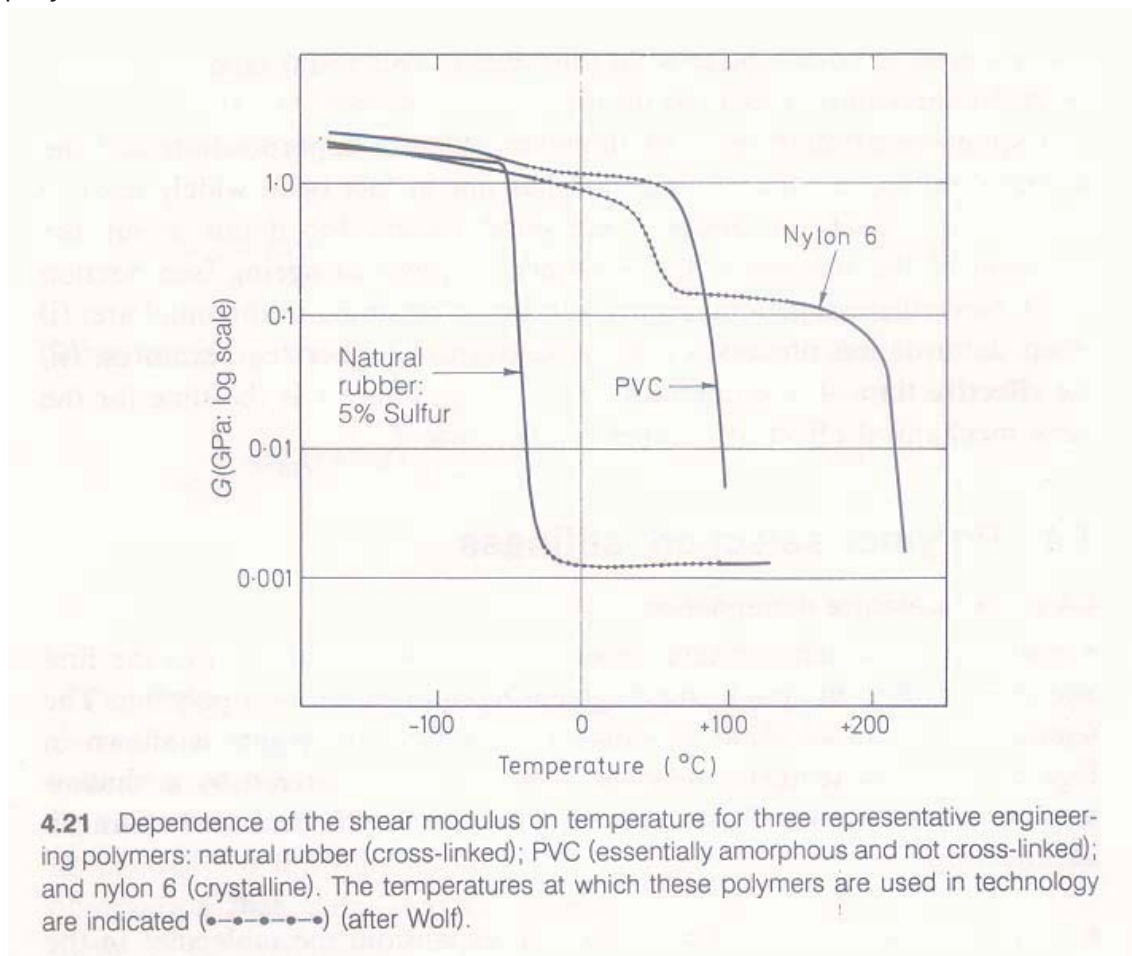


Fig 4.21 here

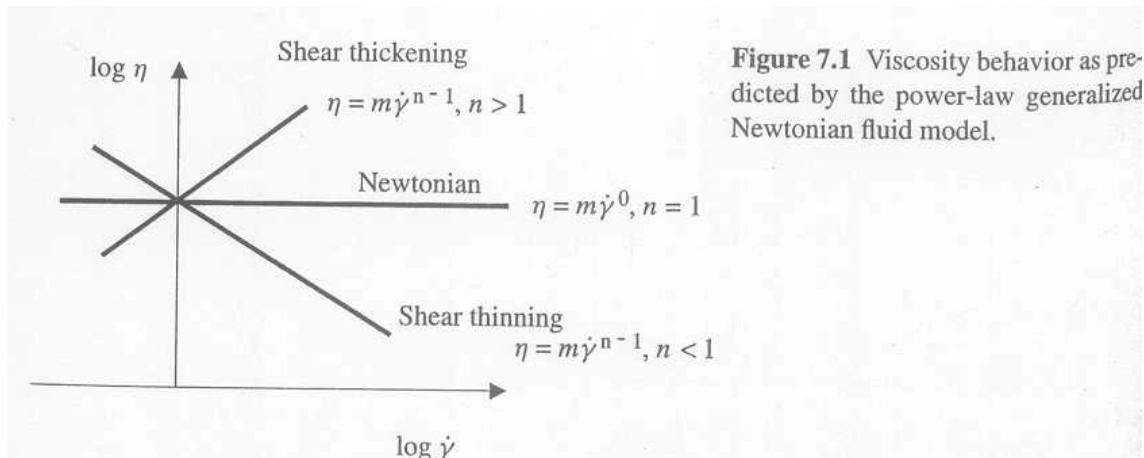
## Constitutive relationship

- ▶ For 100% elastic materials;  
 $\tau = G\gamma, \sigma = E\epsilon \quad (E \cong 3G)$

- ▶ For 100% viscous materials,

$$\tau = \eta \frac{d\gamma}{dt}$$
$$\eta = \text{Constant (Newtonian)}$$
$$\eta = \eta \left( \left| \frac{d\gamma}{dt} \right| \right) \text{ (for non - Newtonian)}$$

(See LN 183 for shear dependent viscosity, especially the power-law model).



## 4.2 Nature of viscoelasticity

### 4.2.1 Creep

A constant stress ( $\sigma = \sigma_0$ ) applied to a polymer sample (viscoelastic material) causes deformation ( $\gamma$ ) which increases with time (=Creep).

$\gamma \propto \text{time}$  (*certain function of*)

$\gamma \propto \sigma$  (*Large stress gives large strain at the same time*)

Then

$$J(t) = \frac{\gamma(t)}{\sigma} \quad (4.3)$$

$J(t) \equiv$  Creep compliance (More concerned with strain as modulus with stress)

Figure 4.1 shows the following linear relationship is hold (linear viscoelasticity).

$$J(t) = \frac{\gamma_1(t)}{\sigma_1} = \frac{\gamma_2(t)}{\sigma_2} \quad (\text{same slope}) \quad (4.2)$$

$J(t)$  is independent of  $\sigma$  but depends on  $t$  (Fig. 4.1d):

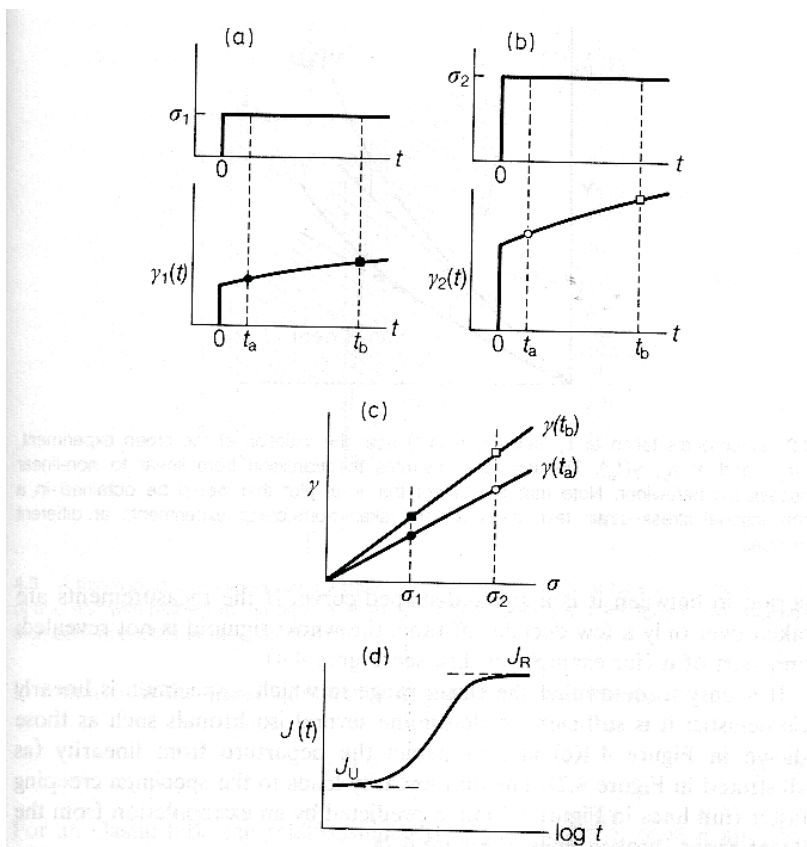
@ low decades of time ( $J_U$ ) and high decades of time ( $J_R$ )  $J$  is almost constant.

@ middle decades of time  $J(t)$  strongly depends on time. (Relaxation)

$J_U \equiv$  Unrelaxed compliance

$J_R \equiv$  Relaxed compliance

The "relaxation" (stress, strain, morphology) is centered at the middle decades of time which corresponds to glass-rubber transition.

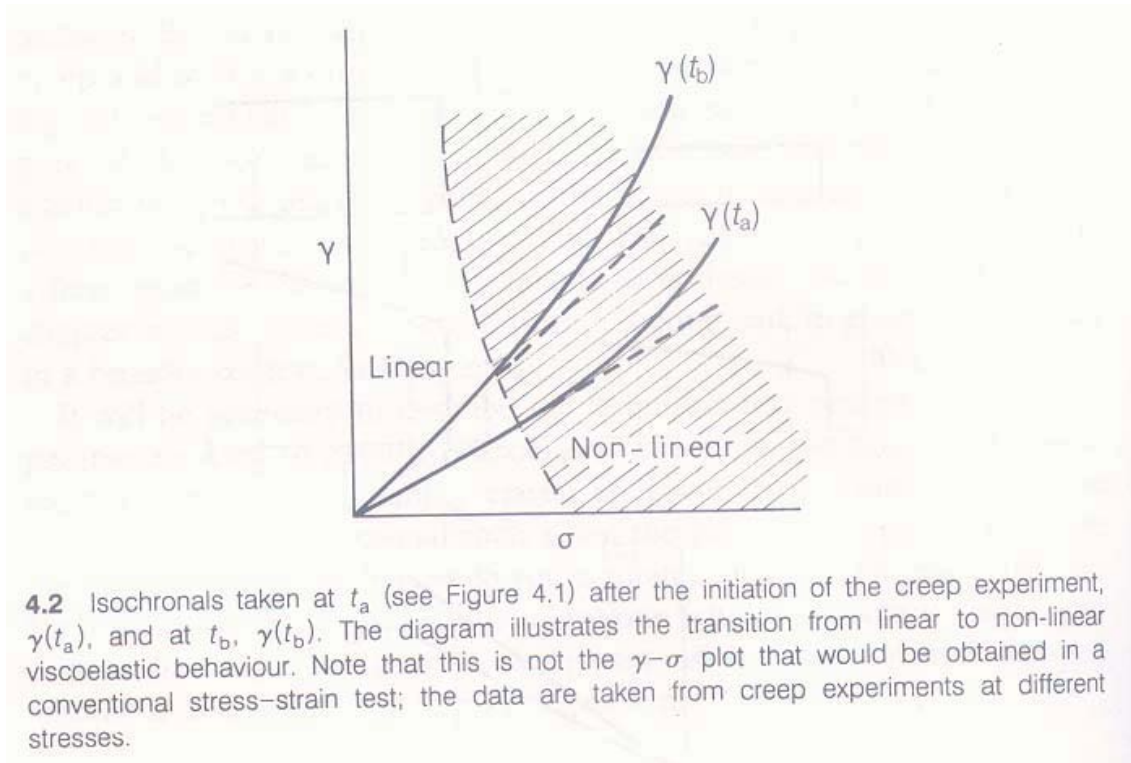


**4.1** Linear viscoelastic creep: (a) constant stress  $\sigma_1$  applied at  $t=0$  leads to time-dependent strain  $\gamma_1(t)$ ; (b) a higher stress  $\sigma_2$  applied at  $t=0$  leads to time dependent strain  $\gamma_2(t)$ ; (c) from (a) and (b) the strains at  $t_a$ ,  $\gamma(t_a)$ , and at time  $t_b$ ,  $\gamma(t_b)$ , are linear in the stress; (d) the observed dependence of  $J(t)$  (eqn 4.3) on  $\log t$  through one complete relaxation.  $J_U$  and  $J_R$  are the unrelaxed and relaxed compliances, respectively.

Note that the linear relationship is hold at small strain (Figure 4.2).

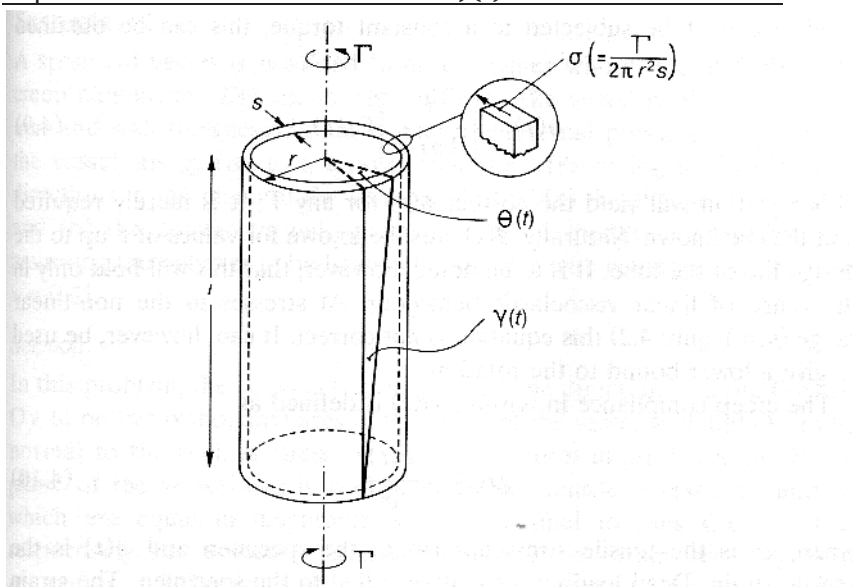
For tensile test the creep compliance is defined as:

$$D(t) = \frac{\epsilon(t)}{\sigma} \quad (10)$$



**4.2** Isochronals taken at  $t_a$  (see Figure 4.1) after the initiation of the creep experiment,  $\gamma(t_a)$ , and at  $t_b$ ,  $\gamma(t_b)$ . The diagram illustrates the transition from linear to non-linear viscoelastic behaviour. Note that this is not the  $\gamma$ - $\sigma$  plot that would be obtained in a conventional stress-strain test; the data are taken from creep experiments at different stresses.

### Experimental determination of $J(t)$ = Thin walled tube



**4.3** A thin-walled tube twisted by a torque  $\Gamma$ : the shear stress in the tube is  $\sigma$ . The rotation of one end with respect to the other is  $\theta$  and the shear strain is  $\gamma$ . If the tube is viscoelastic, then both quantities depend on time,  $\theta(t)$  and  $\gamma(t)$ .

Fig 4.3 here

Thickness of tube wall =  $s \ll \text{radius}(r)$

length =  $l$

Apply constant torque ( $\Gamma$ )

$$\Gamma = (2\pi r s) \sigma * r = 2\pi r^2 s \sigma \quad (4)$$

$$\rightarrow \sigma = \frac{\Gamma}{2\pi r^2 s} \quad (\text{Constant}) \quad (5)$$

Shear strain Changes with time as

$$\gamma(t) = \frac{r\theta(t)}{l} \quad (6)$$

Compliance

$$J(t) = \frac{\gamma(t)}{\sigma} = \frac{\frac{r\theta(t)}{l}}{\frac{\Gamma}{2\pi r^2 s}} = \left(\frac{2\pi r^3 s}{l}\right) \frac{\theta(t)}{\Gamma}$$

As  $t \uparrow \rightarrow \theta(t) \uparrow \rightarrow J(t) \uparrow$

Alternatively in design,  $\theta(t)$  can be predicted using  $J(t)$  data.

#### Ex. 4.1

Specimen length = 200 mm  
 Cross sectional area =  $25 \times 3 \text{ mm}^2$

}  $\xrightarrow{250\text{N}}$  0.5 mm extended in 100s

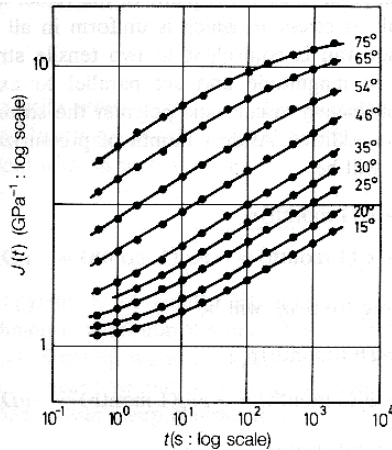
D(100s)?

Solve.  $D(t) = \frac{\epsilon(t)}{\sigma}$

$$\begin{aligned} D(100) &= \frac{\epsilon(100)}{\sigma} = \frac{\frac{l-l_0}{l_0} = \frac{200.5-200}{200}}{\frac{250\text{N}}{(25 \times 3)\text{mm}^2 \left(\frac{1\text{m}}{1000\text{mm}}\right)^2}} = 7.5 \times 10^{-10} \frac{\text{m}^2}{\text{N}} \\ &= 7.5 \times 10^{-10} \frac{1}{\text{Pa}} \frac{10^{10}\text{Pa}}{1\text{GP}} \\ &= 7.5 \text{ GP}^{-1} \end{aligned}$$

Students practice Ex 4.2.

Fig. 4.4 J(t) of linear PE between 15-75°C.



4.4 Shear compliance  $J(t)$  of linear polyethylene at different temperatures in the region of the  $\alpha$ -relaxation. Measurements are taken at times between 0.8 and 2000 s. The data are plotted against  $\log t$ , as a plot against  $t$  will not reveal the significant differences in the shape of the curves at different temperatures (after McCrum and Morris).

Fig. 4.4 here

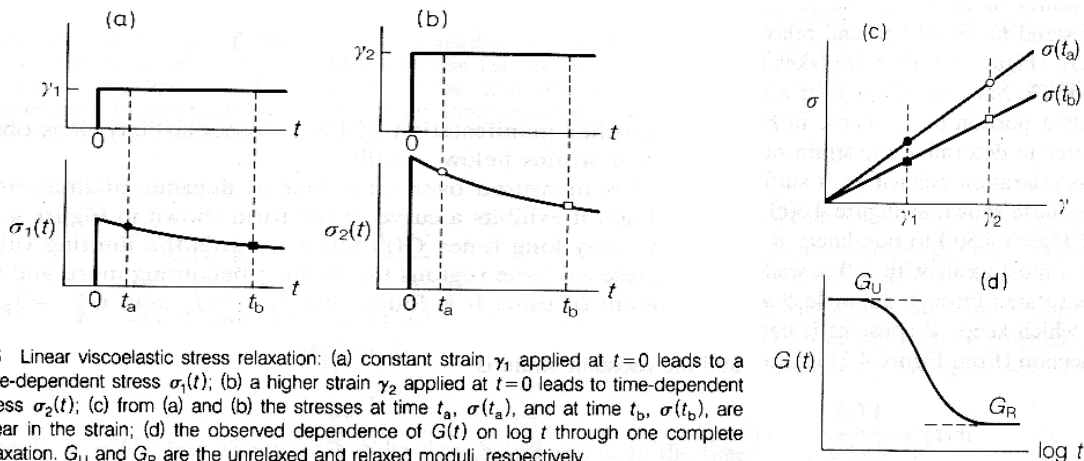
Note : The creep (called  $\alpha$  relaxation) is centered at 46°C, i.e. the slope of  $\log J(t)$  vs  $\log t$  is greater at 46°C than any other temperatures in  $10^{-1} - 10^4$ s (Detailed in 4.3).

→Characteristic relaxation time of chain=Experimental time at 46°C.

#### 4.2.2 Stress Relaxation

Stress rxn : Stress to hold the specimen at constant strain decreases with time.

(Deformed chains are relaxed with time) (See Fig 4.5)



4.5 Linear viscoelastic stress relaxation: (a) constant strain  $\gamma_1$  applied at  $t=0$  leads to a time-dependent stress  $\sigma_1(t)$ ; (b) a higher strain  $\gamma_2$  applied at  $t=0$  leads to time-dependent stress  $\sigma_2(t)$ ; (c) from (a) and (b) the stresses at time  $t_a$ ,  $\sigma(t_a)$ , and at time  $t_b$ ,  $\sigma(t_b)$ , are linear in the strain; (d) the observed dependence of  $G(t)$  on  $\log t$  through one complete relaxation.  $G_U$  and  $G_R$  are the unrelaxed and relaxed moduli, respectively.

Fig 4.5 here (See also 4N3 for plastic bolt)

$$\sigma \propto \gamma$$

$$\sigma(t) = G(t)\gamma \quad G : \text{Shear modulus}$$

$$\frac{\sigma_1(t)}{\gamma_1} = \frac{\sigma_2(t)}{\gamma_2} = G(t) \quad G : \text{Independent of } \gamma$$

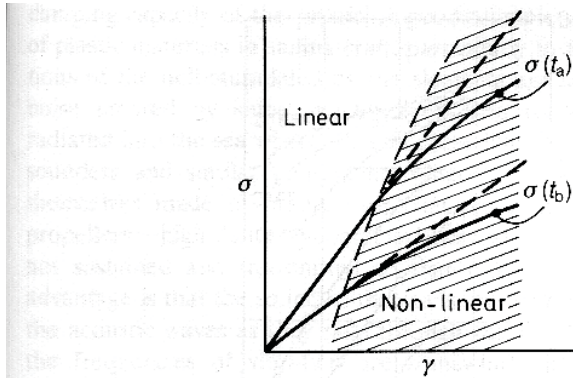


Note  $G_u^{-1} = J_u$      $G_R^{-1} = J_R$

But  $G^{-1} \neq J(t)$  in general

$G(t)$  is determined by the thin wall tube as above for creep.

**Fig. 4.6** Transition from linear to nonlinear stress relaxation behavior



**4.6** Isochronals taken at  $t_a$  (see Figure 4.5) after the initiation of the stress relaxation experiment,  $\sigma(t_a)$ , and at  $t_b$ ,  $\sigma(t_b)$ . The diagram illustrates the transition from linear to non-linear behaviour. Note that this  $\sigma$ - $\gamma$  plot cannot be obtained in a conventional stress-strain experiment: it must be obtained by a series of stress relaxation experiments, as illustrated in Figure 4.5.

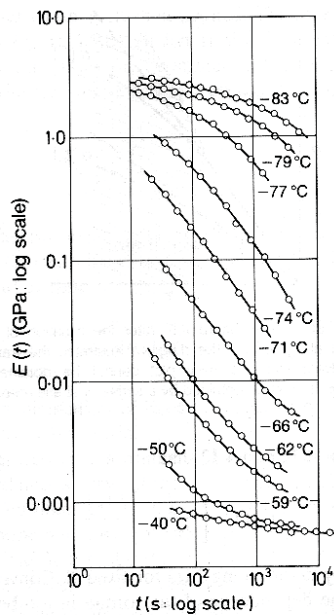
### Stress relaxation modulus for tensile test

$$E(t) = \frac{\sigma(t)}{\epsilon} \quad (14)$$

$$\epsilon = \text{const} \left( = \frac{l-l_0}{l} \right)$$

**Fig. 4.7** Stress relaxation modulus in tension for polyisobutylene

Maximum slope @  $-66^\circ\text{C}$  → Relaxation is centered at  $66^\circ\text{C}$



**4.7** Stress relaxation modulus observed in tension  $E(t)$  of polyisobutylene at different temperatures in the region of the glass-rubber relaxation ( $T_g = -80^\circ\text{C}$ ). At  $-83^\circ\text{C}$  at short time,  $E(t)$  approaches asymptotically the modulus of the glass; at  $-40^\circ\text{C}$  at long time,  $E(t)$  approaches asymptotically the modulus of the rubber. The relaxation is centred in the region of  $-66^\circ\text{C}$ . Note the immense reduction in  $E(t)$  of over 3 decades in a temperature rise of  $43^\circ\text{C}$ : this behaviour is typical of amorphous polymers at the glass-rubber relaxation.

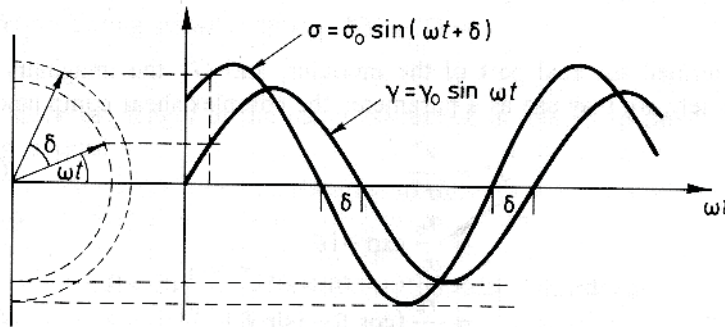
### 4.2.3 Dynamic Properties

Input=Strain  $\xrightarrow{\text{linear viscoelastic range}}$  Output=Stress

$$\gamma = \gamma_0 \sin \omega t \quad (15) \qquad \sigma = \sigma_0 \sin (\omega t + \delta) \quad (16)$$

The output is also sinusoidal but with different phase angle.

Figure 4.8 here



4.8 Vector representation of an alternating stress leading an alternating strain by phase angle  $\delta$ .

#### 2 Extremes

[	100% elastic	$\tau = G\gamma = G\gamma_0 \sin \omega t = \sigma_0 \sin \omega t$	in phase with $\gamma$
	100% viscous	$\tau = \eta \dot{\gamma} = \eta \frac{d\gamma}{dt} = \eta \gamma_0 \omega \cos \omega t$	90° out of phase with $\gamma$

For viscoelastic materials  $0 < \delta < 90^\circ$

Rewrite (16)

Trig identity:  $[\sin(\alpha + \beta) = \sin\alpha\cos\beta + \cos\alpha\sin\beta]$

$$\sigma = \sigma_0 \cos\delta \sin\omega t + (\sigma_0 \sin\delta) \cos\omega t \quad (17)$$

$\sin\omega t$  term: in phase with strain

$\cos\omega t$  : out of phase

$$\sigma = \sigma_1 \sin\omega t + \sigma_2 \cos\omega t \quad (17)'$$

where,  $\sigma_1 = \sigma_0 \cos\delta$  ,  $\sigma_2 = \sigma_0 \sin\delta$

Define

$$G' \equiv \frac{\sigma_1}{\gamma_0} = \frac{\sigma_0}{\gamma_0} \cos\delta \quad (18)$$

$$G'' \equiv \frac{\sigma_2}{\gamma_0} = \frac{\sigma_0}{\gamma_0} \sin\delta \quad (19)$$

Then (17)' becomes

$$\sigma = \gamma_0 (G' \sin\omega t + G'' \cos\omega t)$$



### Complex notations

$$\gamma^* = \gamma_0 e^{i\omega t} \quad (20)$$

Then

$$\sigma^* = \sigma_0 e^{i(\omega t + \delta)} \quad (21)$$

$$\rightarrow G^* = \frac{\sigma^*}{\gamma^*} = \frac{\sigma_0 e^{i(\omega t + \delta)}}{\gamma_0 e^{i\omega t}} = \frac{\sigma_0}{\gamma_0} e^{i\delta} = \frac{\sigma_0}{\gamma_0} (\cos\delta + i\sin\delta) = G' + iG'' \quad (22-24)$$

↑ Phase of modulus is based on strain!

$G^*$  = complex (shear) modulus

$G'$  = storage (shear) modulus

$G''$  = loss (shear) modulus

$$\tan\delta = \frac{G''}{G'} \quad (\text{loss tangent})$$

### Alternatively for Complex compliance

$$\sigma = \sigma_0 \sin\omega t \quad \leftarrow \text{Base phase}$$

$$\gamma = \gamma_0 \sin(\omega t + \delta)$$

$$\rightarrow \gamma = (\gamma_0 \cos\delta) \sin\omega t + (\gamma_0 \sin\delta) \cos\omega t \quad (A)$$

$$= \gamma_1 \sin\omega t + \gamma_2 \cos\omega t \quad (A)'$$

$$\gamma_1 = \gamma_0 \cos\delta$$

$$\gamma_2 = \gamma_0 \sin\delta$$

Define

$$\left. \begin{aligned} J' &= \frac{\gamma_1}{\sigma_0} = \frac{\gamma_0}{\sigma_0} \cos\delta \\ J'' &= \frac{\gamma_2}{\sigma_0} = \frac{\gamma_0}{\sigma_0} \sin\delta \end{aligned} \right\} (B)$$

$$(B) \rightarrow (A)'$$

$$\gamma = \sigma_0 (J' \sin\omega t + J'' \cos\omega t) \quad (C)$$

$$\tan\delta = \frac{J''}{J'} \quad \left( \frac{\text{out of phase amplitude}}{\text{in phase amplitude}} \right)$$

### Complex notation

$$J^* = \frac{\gamma^*}{\sigma^*} = \frac{\gamma_0}{\sigma_0} e^{-i\delta} = \frac{\gamma_0}{\sigma_0} (\cos\delta - i\sin\delta) = J' - iJ'' \quad (25-27)$$

$$\tan\delta = \frac{G''}{G'} = \frac{J''}{J'} \quad \left( \frac{\text{loss part}}{\text{storage part}} \right) \quad (28)$$

$$(J^* = \frac{1}{G^*} \text{ by definition But } J \neq \frac{1}{G} \text{ in general})$$

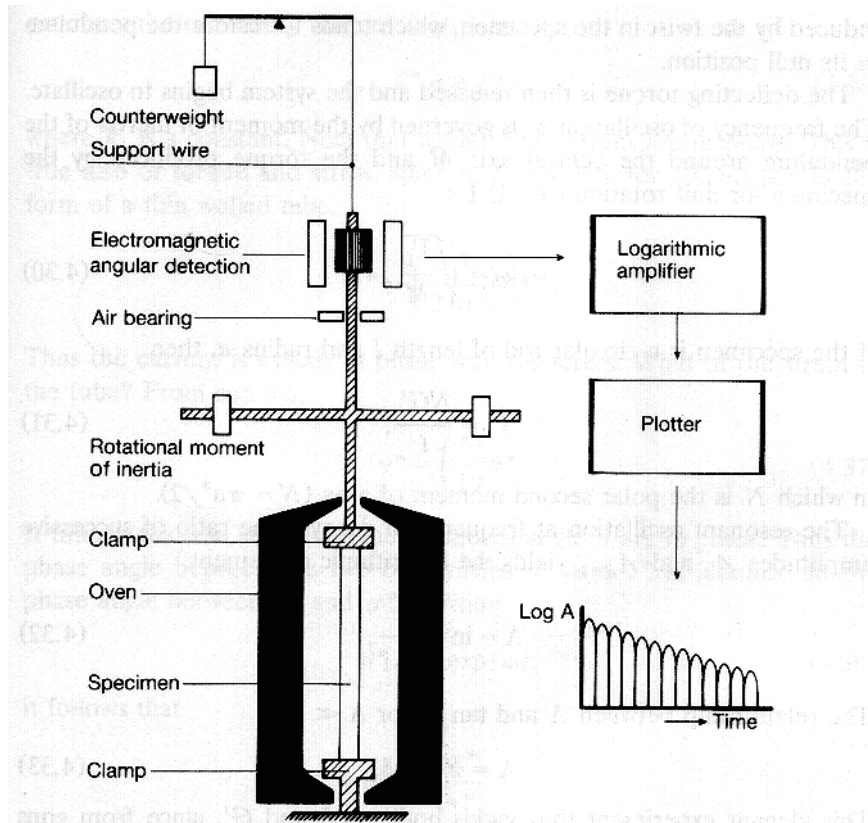
100% elastomer:  $\tan\delta = 0$

As Temp  $\uparrow \rightarrow \tan\delta \uparrow$  (friction  $\rightarrow$  viscous dissipation)

Students practice Ex 4.3.

Determination of complex modulus by torsion pendulum (Figure 4.9)\_

Scan Figure 4.9 here



**4.9** Torsion pendulum for the determination of shear modulus and damping as functions of temperature at frequencies around 1 Hz; the support wire has negligible torsional rigidity (after Struik).

Oscillation frequency ( $\omega$ )

$$\omega = \sqrt{\frac{\Gamma_1}{M}} \quad (4.30)$$

M=Moment of inertia

$\Gamma_1$ =Torque produced by the specimen for unit rotation ( $\Theta=1$ )

$\Gamma_1$  is given by

$$\Gamma_1 = \frac{NG'}{l} \quad (31)$$

where  $N=\pi a^4/2$

The resonant oscillation at frequency  $\omega$  decreases. The ratio of successive amplitude  $A_n$  and  $A_{n+1}$  yields the logarithmic decrement and  $\tan\delta$  as

$$\Lambda = \ln \frac{A_n}{A_{n+1}} \quad (32)$$

$$\Lambda = \pi \tan \delta \quad (33)$$

*Dynamic properties are commonly determined by DMTA (now DMA).-Students will practice DMTA measurements during Polymer Processing Experiment.*

See and interpret dynamic data in [Figures 4.10, 4.11, 4.12](#)

Figure 4.10

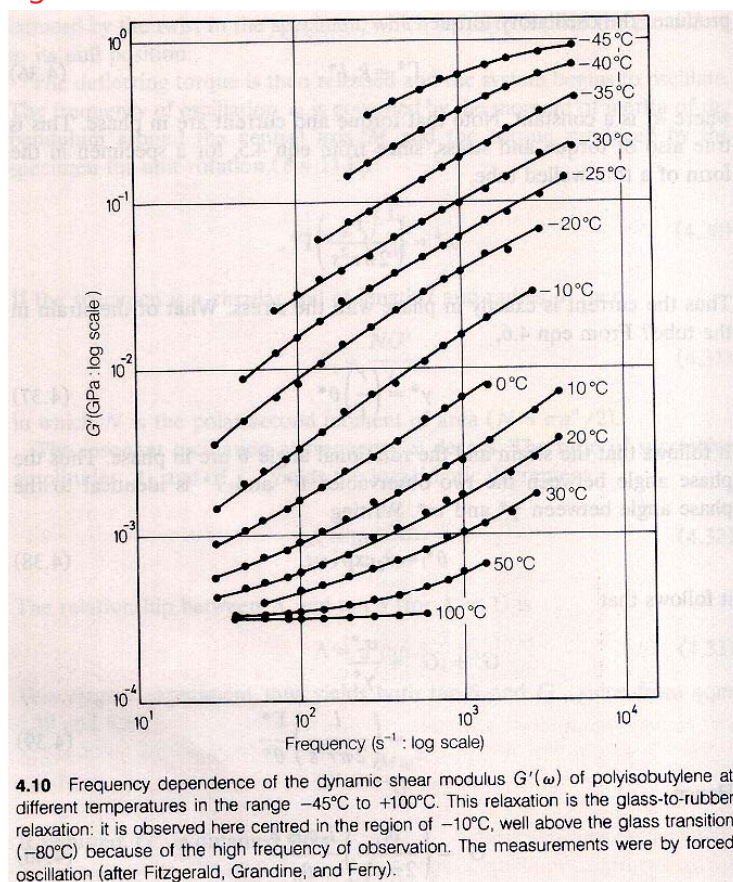
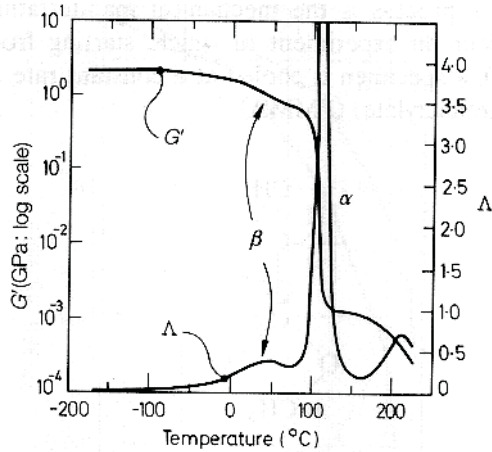
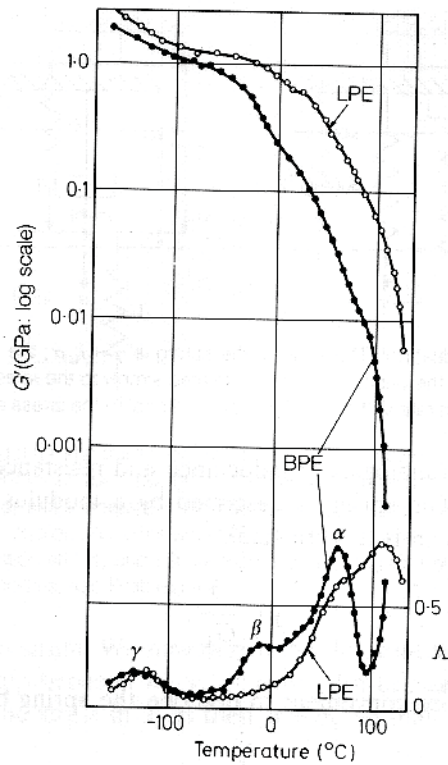


Figure 4.11



**4.11** Temperature dependence of shear modulus  $G'$  and logarithmic decrement  $\Delta$  as a function of temperature for poly(methyl methacrylate) at constant frequency near 1 Hz. The  $\alpha$ -relaxation is due to the onset of movement of the main backbone of the molecule; the  $\beta$ -relaxation is due to the onset of hindered rotation of the side group. The polymer glass, at temperatures where the side group is mobile, is more ductile than at the lower temperatures when its movement is frozen in. Measurements taken by torsion pendulum (after Schrieder and Wolf).

Figure 4.12



**4.12** Temperature dependence of the shear modulus  $G'$  and logarithmic decrement  $\Delta$  of linear (LPE) and branched (BPE) polyethylene. Measurements by torsion pendulum at frequency  $\sim 1$  Hz. The relaxation processes are labelled  $\alpha$  for that at the highest temperature,  $\beta$  for that at the next highest temperature, and so on. The observation of the  $\alpha$ -process in creep for LPE is shown in Figure 4.4 (after Flocke).

## Viscoelastic Model

### Maxwell model (Series)

$$\begin{aligned} \text{Spring: } \sigma_1, \epsilon_1 & \quad \sigma_1 = E\epsilon_1 \\ \text{Dash pot: } \sigma_2, \epsilon_2 & \quad \sigma_2 = \eta \frac{d\epsilon_2}{dt} \end{aligned}$$

$$\begin{aligned} \sigma &= \sigma_1 = \sigma_2 \\ \epsilon &= \epsilon_1 + \epsilon_2 \end{aligned}$$

### Differentiation

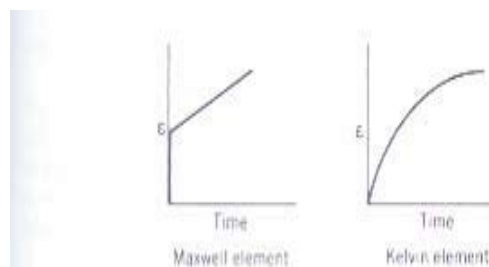
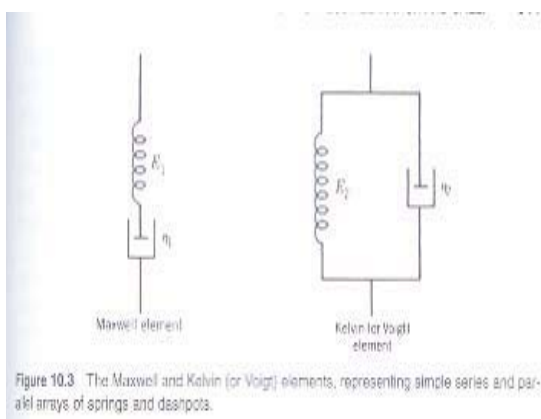
$$\begin{aligned} \frac{d\epsilon}{dt} &= \frac{d\epsilon_1}{dt} + \frac{d\epsilon_2}{dt} = \frac{1}{E} \frac{d\sigma_1}{dt} + \frac{1}{\eta} \sigma_2 \\ \rightarrow \frac{d\epsilon}{dt} &= \frac{1}{E} \frac{d\sigma}{dt} + \frac{1}{\eta} \sigma \quad \leftarrow (\sigma_1 = \sigma_2 = \sigma) \quad \text{D.E for Maxwell model} \quad (1) \end{aligned}$$

### For creep

$$\sigma = \sigma_0 \quad (\text{Imposed}) \Rightarrow \frac{d\sigma}{dt} = 0 \quad @ \quad (1)$$

How does  $\epsilon(t)$  change with time ?

$$\begin{aligned} \frac{d\epsilon}{dt} &= \frac{1}{\eta} \sigma_0 \Rightarrow \int_{\epsilon_0}^{\epsilon} d\epsilon = \int_0^t \frac{\sigma_0}{\eta} dt' \\ \epsilon - \epsilon_0 &= \frac{\sigma_0}{\eta} t \Rightarrow \epsilon = \epsilon_0 + \frac{\sigma_0}{\eta} t \quad \epsilon_0 = \frac{\sigma_0}{E} \quad (\text{i.c.}) \\ \epsilon &= \epsilon_0 + \frac{\epsilon_0 E}{\eta} t = \epsilon_0 \left(1 + \frac{t}{\tau}\right) \\ @t = \tau, \epsilon &= 2\epsilon_0 \end{aligned}$$



Spurling Fig 10.3 & 10.4 here

### Stress relaxation

$$\epsilon(t) = \epsilon_0 = \text{const, we look at } \delta(t) ?$$

$$\frac{d\epsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

$$\frac{d\epsilon}{dt} = 0 \text{ for stress relaxation experiment}$$

$$\frac{1}{E} \frac{d\sigma}{dt} = -\frac{\sigma}{\eta}$$

$$\frac{d\sigma}{\sigma} = -\frac{E}{\eta}$$

$$\ln \sigma \Big|_{\sigma_0}^{\sigma} = \int_0^t -\frac{E}{\eta} dt = -\frac{E}{\eta} t + 0$$

$$\ln \frac{\sigma}{\sigma_0} = -\frac{E}{\eta} t = -\frac{t}{\tau} \rightarrow \sigma = \sigma_0 e^{-\frac{t}{\tau}} \quad (\sigma_0 = E\epsilon_0)$$

$$\left( \tau = \frac{\eta}{E} = \text{relaxation time} \right)$$

$$\tau [=] \frac{\eta [=] \frac{M}{Lt}}{E [=] \frac{M}{L^2}} = \frac{M L^2 t^2}{Lt ML} = t \quad \leftarrow \text{so } \tau \text{ is called relaxation time}$$

### Voigt model

$$\text{Spring (elastic)} \quad \sigma_1 = E\epsilon_1$$

$$\text{Dashpot (viscous)} \quad \sigma_2 = \eta \frac{d\epsilon_2}{dt}$$

$$\sigma = \sigma_1 + \sigma_2$$

$$\epsilon = \epsilon_1 = \epsilon_2$$

$$\sigma = \sigma_1 + \sigma_2, \quad \sigma = E\epsilon + \eta \frac{d\epsilon}{dt} \quad (\epsilon = \epsilon_1 = \epsilon_2)$$

DE for Voigt

### Creep analysis

$$\sigma = \sigma_0 = \text{const} \quad \epsilon(t) ?$$

$$(\sigma_0 - E\epsilon) dt = \eta d\epsilon, \rightarrow \frac{E}{\eta} (\frac{\sigma_0}{E} - \epsilon) dt = d\epsilon$$

$$\frac{E}{\eta} dt = \frac{d\epsilon}{(\frac{\sigma_0}{E} - \epsilon)}$$

Integration

$$\frac{E}{\eta} \int_0^t dt = \int_0^{\epsilon} \frac{d\epsilon'}{(\frac{\sigma_0}{E} - \epsilon')} \xrightarrow{\int \frac{d\epsilon}{(\frac{\sigma_0}{E} - \epsilon)} = -\ln(\frac{\sigma_0}{E} - \epsilon)} \left( \frac{E}{\eta} \right) t = \ln \left( \frac{\sigma_0/E}{\frac{\sigma_0}{E} - \epsilon} \right)$$

$$\left( \frac{E}{\eta} t = \frac{t}{\tau}, \frac{E}{\eta} = \frac{1}{\tau}, \frac{\sigma_0}{E} = \epsilon_0 \right)$$

$$\Rightarrow \frac{t}{\tau} = \ln \left( \frac{\sigma_0/E}{\frac{\sigma_0}{E} - \epsilon} \right) \rightarrow \frac{\sigma_0/E}{\frac{\sigma_0}{E} - \epsilon} = e^{\frac{t}{\tau}}$$

$$\frac{\sigma_0}{E} = (\frac{\sigma_0}{E} - \epsilon) e^{\frac{t}{\tau}}$$

$$\left( \frac{\sigma_0}{E} \right) e^{-\frac{t}{\tau}} = (\frac{\sigma_0}{E} - \epsilon)$$

$$\text{So, } \epsilon = \frac{\sigma_0}{E} - \left( \frac{\sigma_0}{E} \right) e^{-\frac{t}{\tau}} = \frac{\sigma_0}{E} (1 - e^{-\frac{t}{\tau}}) \quad \left( = \epsilon_0 (1 - e^{-\frac{t}{\tau}}) @t = 0, \epsilon = 0 \right)$$